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PARTICULARITIES OF SINTERING OF CERAMIC PASTES CONTAINING MAGNESIUM SILICATES

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The results of a study of the behavior of samples based on clays with different chemical – mineralogical compositions a component containing natural magnesium silicates attest to the active participation of dunite byproducts from mining-enrichment operations in the formation of the properties of decorative-finishing building ceramic during calcination.

Articles made of decorative-finishing ceramic are characterized by a complex of physical – mechanical properties which must not change during use. The density, strength, heat-resistance, and other properties are determined by the phase composition of the ceramic, structure formation processes, and crystal sizes, all of which are closely associated with the change of the microstructure of the material during calcination. One way to regulate the phase-formation processes and degeneration of the structure during heat-treatment is to use an artificial, rationally chosen, charge. Previous work has established that the byproducts, containing magnesium silicates, from mining – enrichment operations actively participate in the thermal synthesis of new crystalline phases — magnesium silicates and aluminosilicates [1].

We have investigated a two-component paste consisting of a plastic component (clays from the Orenburg region) and nonplastic component (dunites, byproducts of the Don Mining – Enrichment Works, located on the territory of the Kempirsai Massive of the Southern Urals). Press powders containing 10 – 70%[2] magnesium-containing technogenic initial material were prepared by optimizing the composition of the charge for the investigations. The initial materials, mixtures, and samples were prepared by the standard method. The physical – mechanical properties of the experimental articles after calcination are presented in Table 1.

The degree of sintering, the effect of a component, and the content of natural magnesium silicates on the kinetics of crystallization, and the general character of the change of the structure were evaluated indirectly according to the water absorption, the total shrinkage, the density, and the compression strength of the material obtained.

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[2] Here and below: mass content.

Analysis of the experimental data (see Fig. 1) shows that water absorption of the clays studied at calcination temperature 1000 – 1200°C is (%): 12.7 – 4.7 Sol'-Iletskoe, 13.8 – 4.9 Chernorechenskoe, and 16.2 – 12.8 Kumakskoe. It should be especially noted that the total shrinkage is high —

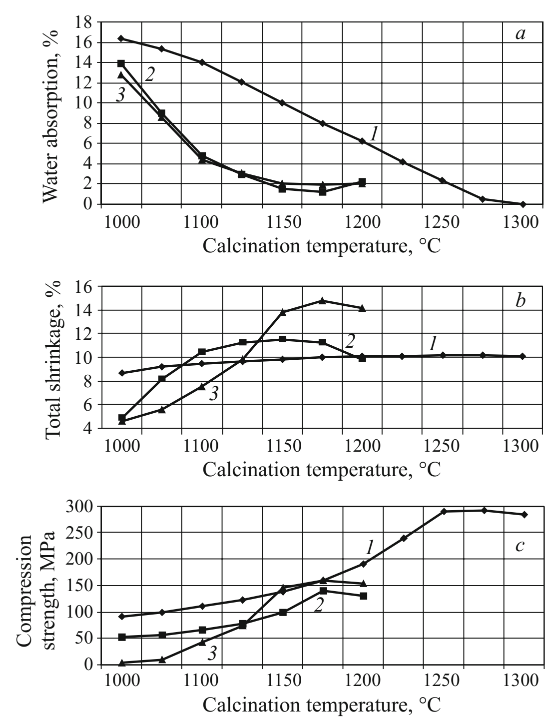

Fig. 1. Variation of the properties of clays from the Orenburg deposits as a function of the calcination temperature: *a*) water absorption; *b*) total shrinkage; *c*) compression strength; *1*, *2*, *3*) clays from the Kumakskoe, Chernorechenskoe, and Sol'-Ileteskoe deposits, respectively.

TABLE 1.

Charge composition, %		Calcination temperature, °C, articles prepared using initial materials from different deposits									
dunites	clay	Sol’-Iletskoe			Chernorechenskoe			Kumakskoe			
		1000	1100	1200	1000	1100	1200	1000	1100	1200	1300
					Water absorption, %						
70	30	21.20	15.60	11.50	20.10	13.60	9.00	22.07	18.40	13.50	7.40
50	50	20.30	12.40	8.00	17.50	10.90	5.10	20.51	16.00	10.70	4.10
30	70	18.70	9.60	4.70	15.50	8.90	2.00	19.70	15.50	10.60	3.34
10	90	16.30	7.06	0	14.20	7.40	0	19.50	15.09	9.40	1.50
					Density, g/cm^3						
70	30	1.70	1.78	1.84	1.71	1.75	1.86	1.62	1.70	1.83	2.00
50	50	1.77	1.82	1.88	1.74	1.79	1.93	1.61	1.71	1.85	2.05
30	70	1.81	1.87	1.92	1.78	1.86	2.00	1.58	1.72	1.89	2.10
10	90	1.83	1.91	1.97	1.83	1.95	2.09	1.54	1.72	1.92	2.17
					Compression strength, MPa						
70	30	2	24	62	15	37	61	22	33	42	166
50	50	4	29	86	20	46	82	42	55	81	211
30	70	6	36	114	28	58	108	62	82	114	249
10	90	9	41	146	38	73	139	86	114	141	281
					Total shrinkage, %						
70	30	1.5	4.9	6.5	1.5	6.2	7.8	1.3	3.4	6.4	7.3
50	50	2.3	6.2	8.5	3.3	7.6	8.7	1.9	4.9	7.9	8.0
30	70	2.7	7.3	9.9	4.1	8.7	9.6	2.4	6.1	8.5	8.8
10	90	3.0	7.8	11.0	4.7	9.4	11.3	2.5	7.2	9.0	9.7

3.5 – 10.5% — for all clays studied. At the same time the total shrinkage of dunites at the same temperatures is 1.0 – 3.5% and the water absorption is 25 – 20%. Consequently, the introduction of magnesium-containing byproducts into the charge results in some increase of the water absorption of all samples studied (see Table 1). It can be supposed that this is determined by the behavior of the dunites during heat treatment. So, at calcination temperatures 500 – 1000°C the degree of fissuring of the rock and the open porosity both increase. Consequently, as the fraction of the technogenic initial material containing magnesium silicates in the charge increases, the open porosity of the entire ceramic article increases irrespective of the properties of the clay component.

Just as in the case of the Kumakskoe clay, articles with water absorption less than 16% could not be obtained from charges based on Sol’-Iletskoe clay and dunite byproducts at 1000°C. This is explained by the refractoriness of its properties and dunites. At the same time a decrease of the dunite content to 40% in the charges based on the Chernorechenskoe clay makes it possible to attain the required water absorption in articles made of the decorative-finishing ceramic. The enlargement of pores in dunites impedes the development of cracks at temperatures 1100 – 1200°C. The identical processes are also observed in this temperature range in the structure of ceramic articles based on the clays studied. At calcination temperature 1100°C the water absorption of the articles decreases to 15.6% in pastes made from Sol’-Iletskoe clay and to 13.6% for Chernorechenskoe clay with the highest dunite content (70%), and for Kumakskoe clay it decreases to 16.0% with byproduct content up to 40%.

Analysis of the results shows that the working interval of calcination of articles can be increased from 50 – 90 to 200 – 300°C and marginal clays with a narrow calcination interval can be used in production by introducing in the ceramic charge byproducts containing magnesium silicates.

A change in the porosity of dunites affects their density and strength. The average density of uncalcined magnesium-containing technogenic initial material is 2.5 g/cm^3. Structural changes in the temperature interval 200 – 1000°C determine the decrease of this characteristic to 1.62 g/cm^3. The formation at 800 – 1000°C of a liquid phase even in negligible amounts (according to petrographic analysis) in the dunites themselves as well as in the clay component promotes partial filling of cracks by the silicate melt, impeding crack development in the grains of the byproduct, and decreases the distance between the particles of the ceramic paste. This increases the density of the material. It is evident from Table 1 that as the dunite content in the charge decreases to 10% and at calcination temperature 1000°C the density of the ceramic articles increases — up to 1.83 and 1.93 g/cm^3 for articles based on Sol’-Iletskoe and Cherno-

rechenskoe clays. The densification of the material can be explained by the fact that the Sol'-Iletskoe and Chernorechenskoe clays, being low-melting, contain a considerable quantity of fluxes. The enrichment of the glass phase with low-valence sodium and potassium ions increases the amount of the phase.

At the same time, the melt interacts with the surface of the dunite grains, drawing them into chemical processes which result in the formation of silicates and aluminosilicates. These crystalline embryos promote densification and hardening of the ceramic articles. Thus, for 70% content of dunite initial material in the charge with calcination temperature 1100°C it is possible to obtain material with density 1.78 g/cm^3 using Sol'-Iletskoe clay, 1.75 g/cm^3 with Chernorechenskoe clay, and 1.70 g/cm^3 with Kumakskoe clay. At the present time, according to the standards, the average density of the articles made of construction ceramic is 1.7 – 2.0 g/cm^3 depending on their purpose. Thus, the density of the material obtained on the basis of technogenic initial material containing magnesium silicates satisfies the demands of the modern construction industry.

The decrease of the strength of samples with increasing amounts of the byproducts in the charge consisting of all clays studied explains the retention of the fissured and porous structure in dunites up to temperatures 1000 – 1100°C. However, even at 1000°C and with 70% dunite content it is possible to obtain articles from construction ceramic, based on the Chernorechenskoe and Kumakskoe clays, which is characterized by a quite high compression strength (see Table 1) — 15 and 22 MPa, respectively.

In the case of articles made of the Sol'-Iletskoe clay, because of its high sand content and low plasticity, a strength 24 MPa was obtained with 70% dunite content and calcination temperature 1100°C. Slow growth of density and strength of pastes containing magnesium silicates or even a small decrease of these properties at calcination temperatures up to 800°C and the preservation of the porous structure of the ceramic improve its filtration power. This makes it possible to regulate the rate of vapor formation inside the material and avoid fracture of the articles, which is especially characteristic for rapid calcination regimes. The introduction of dunite byproducts into the paste made it possible to eliminate swelling and drop-off of strength, which is characteristic for samples made from clean clays (see Fig. 1*a* – *c*).

The removal of mechanically admixed and chemically bound water as well as crystallization embryos and the appearance of the silicate melt change the dimensions of ceramic articles. The products of thermal decomposition of the dunite initial material and the synthesized magnesium silicates and aluminosilicates, being thermally stable at high temperatures, create a framework which impedes intense development of shrinkage and promotes the preservation of the shape imparted to the article.

The total shrinkage of the Sol'-Iletskoe, Kumakskoe, and Chernorechenskoe clays at calcination temperature 1000°C is 3.4, 8.66, and 4.8%, respectively. When 10% dunites are added to the charge based on these clays with the same calcination temperature, the total shrinkage decreases to 3.0, 7.2, and 4.7%, respectively, and for 70% content of magnesia initial material in the paste the shrinkage decreases to 1.5, 3.4, and 1.5%, respectively. When the calcination temperature increases to 1100°C, the total shrinkage of the clean clays increases to 8.2% for Sol'-Iletskoe, to 9.5% for Kumakskoe, and to 10.4% for Chernorechenskoe. The use of a magnesium-containing component in an amount equal to 10% at a given temperature decreases the shrinkage of the samples based on the clays indicated above to 7.8, 9.0, and 9.4%, and for 70% dunite content the increase of the total shrinkage slows down to 4.9, 6.0, and 6.8%, respectively.

In summary, the data obtained in a study of the behavior of samples based on a component containing natural magnesium silicates and clays with different chemical-mineral compositions show that dunite byproducts actively participate in the formation of the properties of decorative-finishing construction ceramic during calcination.

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